Computational and Theoretical Chemistry 1123 (2018) 149–153

Contents lists available at ScienceDirect

Computational and Theoretical Chemistry

journal homepage: www.elsevier.com/locate/comptc

An alternative approach to structural analysis for gas electron diffraction method

Yuriy A. Zhabanov *, Alexander E. Pogonin

Ivanovo State University of Chemistry and Technology, Research Institute of Chemistry of Macroheterocyclic Compounds, Sheremetev av. 7, 153000 Ivanovo, Russian Federation

ARTICLE INFO

Article history:
Received 4 October 2017
Received in revised form 30 November 2017
Accepted 30 November 2017
Available online 1 December 2017

A novel approach to the inverse problem solution in gas electron diffraction is reported. It involves the variation of force-constants scale factors instead of "classical" variation of vibrational amplitudes. Resulting force-constants scale factors are used for the amplitudes and vibration corrections calculations. The algorithm and software have been successfully tested. For this purpose, experimental gas electron diffraction data were employed to obtain structural parameters and these parameters were compared to available ones of benzene, iodine and copper octamethylporphyrin molecules.

Gas electron diffraction (GED) is an experimental method to obtain the structures of free molecules. The possibility of studying molecular structure of large molecules by the synchronous gas-phase electron diffraction and mass spectrometry (GED/MS) is demonstrated on several examples [1–3] including porphyrins [4–7], phthalocyanines [8,9] and porphyrazine [10]. The GED structural analysis is based on the inverse problem solution for the determination molecular structures by means of the diffraction patterns refinement. It implies fitting of the molecular model to experimental data by variation of the internuclear distances and vibration amplitudes (l) of the atom pairs.

The starting geometrical parameters (bond distances, valence angles) can be obtained by quantum chemical calculations. The starting vibrational amplitudes (l_{theor}) can be calculated on the base of force field obtained from quantum chemical calculations with the use of the algorithms developed in the works [11–14]. During the refinement of GED data the kits of internuclear distances and vibrational amplitudes are combined into groups. The differences between the values of similar distances and amplitudes are fixed within the groups [15]. The data of microwave, IR and Raman spectroscopy can be involved into processing the GED experimental results. This method of processing was demonstrated in works [16,17]. Furthermore, the authors of [16,17] used not only data from other experimental methods in GED structural analysis, but also carried the variation of Pulay coefficients [18]. However, the authors of these works have studied only the structure of relatively small objects, i.e. benzene in [16] and 4-fluorobenzaldehyde in [17].

In this manuscript, we are describing the realization of the novel approach to the GED inverse problem solution that involves the variation of force-constants scale factors used for the amplitudes and vibration corrections calculations instead of variation of the vibrational amplitudes.

Structural analysis is based on a comparison of experimental and theoretical $sM(s)$ molecular intensity functions of electron scattering with the help of the least squares method. The quadratic functional for minimization is

$$Q = \sum_{s} \omega_s \left[sM_{\text{exp}}(s) - ksM_{\text{theor}}(s) \right]^2$$

where s is a scattering angle, ω_s is a weight function, k is a scaling factor, $sM(s)_{\text{exp}}$ is a experimental molecular intensity, obtained by diffraction patterns refinement, $sM(s)_{\text{theor}}$ is a theoretical molecular intensity, which is calculated by the formula

$$sM_{\text{theor}}(s) = \sum_{i>j}^{N} \sum_{j=1}^{N} g_{ij}(s) \exp\left(-\frac{l_{ij}^2 s^2}{2} \right) \frac{\sin\left(s(r_{ij} - k_{ij} s^2) \right)}{r_{ij}}$$

where r_{ij} is a thermally average internuclear distance of the pair of atoms i and j (r_a), l_{ij} is a vibrational amplitude of atom pairs, s is a scattering angle parameter and $g_{ij}(s)$ is a function characterizing a scattering ability, $k_{ij} = \frac{1}{6} a_{ij} l_{ij}^4$ – phase-shift parameter, a_{ij} – asymmetry constant. Thus, the aim of structural analysis is minimization of Q functional by r_{ij} and l_{ij} variation of molecular models.

It is known that the thermally average r_a distances are not geometrically consistent [11]. Therefore, in current practice GED structural analysis are internally done in terms of geometrically

* Corresponding author.
E-mail address: zhabanov@isuct.ru (Y.A. Zhabanov).

https://doi.org/10.1016/j.comptc.2017.11.024
2210-271X/

consistent r_{h1} (the internuclear distances are obtained using the vibrational corrections calculated on base of harmonic force field assuming the nonlinear dependence of the internal and Cartesian coordinates) or r_e (equilibrium distances) parameters [19]. It requires corresponding corrections to interatomic distances ($r_{h1}-r_a$) or (r_e-r_a) and starting values of vibrational amplitudes l, which are, in most cases, computed on the basis of theoretically calculated force constants. The calculated amplitudes and vibration correction values can be changed with the use of the approach of force constants scaling proposed by Pulay [18].

$$f_{ij}(p) = p_i^{1/2} p_j^{1/2} f_{ij}^0$$

where f_{ij}^0 is a force constant, p_i and p_j are scaling factors. A new program GedModule has been written to realize a new approach of GED structural analysis, which uses the variation of the Pulay scale factors [18] instead of variation of the vibrational amplitudes.

The algorithms of "classical" and new alternative approaches are shown in Fig. 1. The new alternative approach involves the recalculation of the amplitudes and vibrational corrections with different values of scaling factors p at every variation step in the structural analysis. Thus, potential energy surface (PES) is exposed

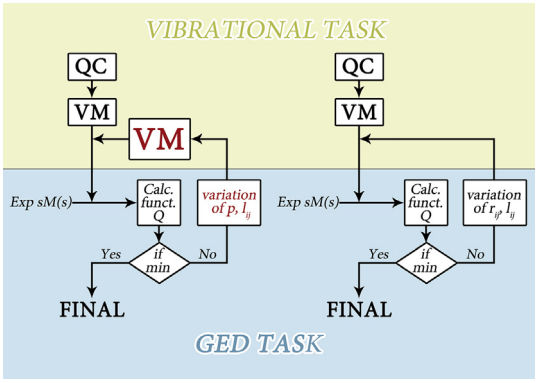

Fig. 1. The algorithms of new alternative (left) and "classical" (right) approaches to the gas electron diffraction inverse problem solution. QC – the quantum chemistry calculations for geometry parameters and force field of a molecule. VM – the process of obtaining the vibrational characteristics of a molecule with the help of VibModule [22] program.

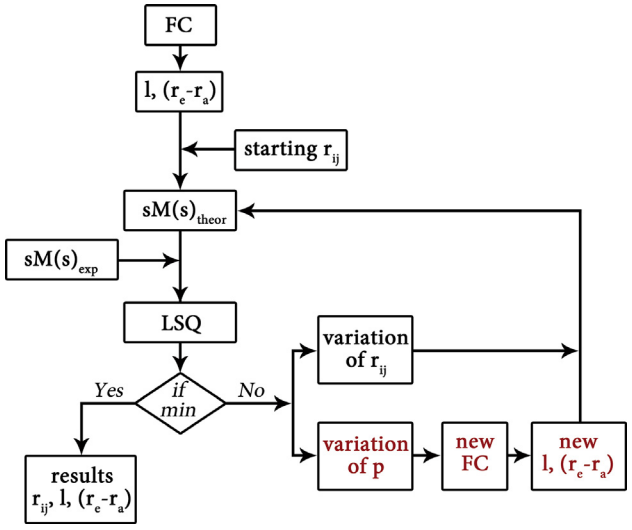

Fig. 2. The algorithm of new alternative approach. FC – force constants matrix (force field); LSQ - least squares, a technique of equation fitting.

to fit the experimental data. The new program GedModule is coded in C++ computer language and uses *GNU Scientific Library* [20] and UNEX mathematical library (UML) from UNEX2 project [21].

Moreover, GedModule contains the code of VibModule program [22], which utilizes Sipachev's algorithms [11–14] for calculating the vibrational amplitudes and corrections. Thus, GedModule performs the variation of Pulay scale factors, recalculates the vibrational amplitudes and corrections and uses them in calculation $sM_{theor}(s)$. The scheme of this developed algorithm is shown in Fig. 2. The actions, mentioned above, are more justified theoretically in the minimisation of Q functional. In this case fitting of the molecular model to the experimental data is performed by force field scaling. Further on, the scaled force field is used to recalculate the vibrational amplitudes. Moreover, in the process of structural analysis the vibrational corrections are being recalculated and updated. According to the classical approach the vibrational corrections were constant during the structural analysis.

In order to test the accuracy of results, obtained with the help of GedModule, structural parameters of several molecules have been defined with the use of experimental GED data for iodine (I_2) [26], benzene (C_6H_6) [26] and 2,3,7,8,12,13,17,18-octamethylporphyrin copper ($CuN_4C_{28}H_{28}$, CuOMP, see Fig. 3) [4]. Further on, the results, obtained by the novel approach will be called "our data".

The electron diffraction patterns of I_2, C_6H_6 and $CuN_4C_{28}H_{28}$ were obtained in a synchronous gas electron diffraction experiments carried out with the use of the EMR-100/APDM-1 unit [23–25]. The results of GED investigations (based on classical approach) of iodine, benzene [26] and CuOMP [4] (Fig. 3) molecular structures were published.

The obtained structural parameters for iodine molecule (I_2) and benzene molecule (C_6H_6) are summarized in Table 1. The values of well-definable distances (such as r(C—C) in benzene, and r(I—I) in I_2) in our refinements are in excellent agreement with the data available in the literature [26–31] (the maximal difference between our results and literature data is 0.001 Å, see Table 1) In the case of benzene, we used three quantum chemical approximations B3LYP/cc-pVTZ, PBE/6-31G and HF/3-21G, see Table 1) for obtaining starting geometry and force field for structural analysis. In all three cases (even in the case of low level HF/3-21G calculation) the same values of bond distance r(C—C) and amplitude l (C—C) were obtained.

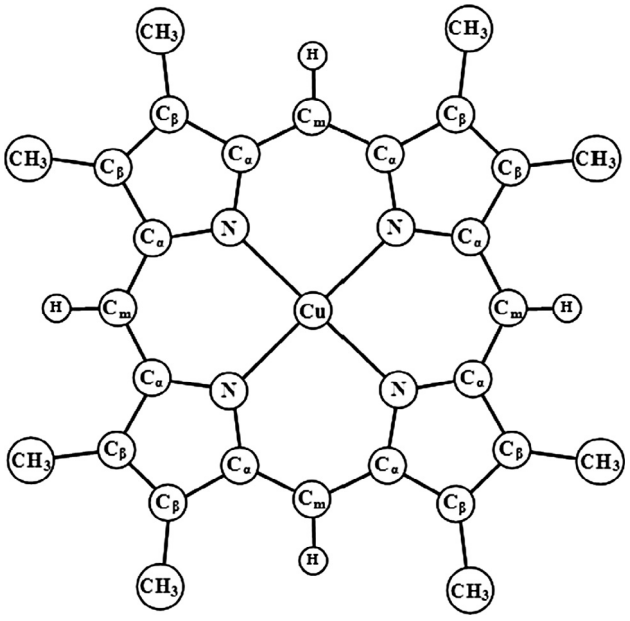

Fig. 3. Molecular structure of the CuOMP.